HIGH TIME RESOLUTION SPECTROSCOPY STUDIES OF THE EXPLOSIVE DECOMPOSITION OF SILVER AZIDE

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We have analyzed the existing assumptions about the mechanism of the explosive decomposition of the heavy metal azides. We present here a study of the kinetics of the explosive decomposition of silver azide, initiated by a laser pulse. New effects are identified and studied, including a pre-explosion conductivity and luminescence. On the basis of our results, we conclude that the reaction proceeds by a chain reaction mechanism. In terms of band theory, we propose a model of the primary chain step of the reaction as the creation of a quasilocalized state deep in the valence band with two holes localized at a defect ($N_3^-$), with impact ionization occurring as they "float up."

INTRODUCTION

The heavy metal azides, a typical one being silver azide ($\text{AgN}_3$), are initiating explosive materials and over the course of several decades they have served as model system for the study of this class of materials.

Even in 1960 a large amount of work had accumulated on the physics and chemistry of these systems, and served as the basis of assumptions as to the mechanism of their explosive decomposition (see the reviews [1, 2]). However, despite that fact, a whole series of questions which are not only important but, in many cases, fundamental ones, remain controversial even to this day, related to the mechanism of this decomposition. In some cases, they have not even yet been formulated.

The reason for this state of affairs, which is at first glance rather paradoxical, lies in the following.

First, the vast majority of the works are devoted to study of the final products and to a series of integral characteristics of the process, which lie rather far from the physics of the primary action. Such a situation is favorable for the postulation of various thought models and discussion, but it does not facilitate the construction of an adequate physical picture of the process.

Second, a large fraction of the studies of the explosive decomposition of heavy metal azides have been carried out by chemists and have been analyzed, mainly, in terms of assumptions drawn from studies of corresponding processes in gases and liquids [1, 2]. The solid state effects have been taken into account in many cases rather approximately, so that there has often been difficulty in "translating" the language of chemical reactions into the language of band systems. Thus, for example, in the excellent monograph [3] the recombination (?) of two holes (NO$_3$ radicals) as they meet is discussed.

In connection with the foregoing discussion, in the present work we analyze the assumptions about the explosive decomposition mechanism, attempting to delineate and to formulate the fundamental unclear questions, and we discuss the data obtained recently by pulse techniques, which makes it possible to answer, albeit in preliminary form, a portion of those questions. We pay special attention to the validity of the "translation" from the language of chemical reactions to the language of solid state physics, in particular that of band theory.
1. FUNDAMENTAL ASSUMPTIONS ABOUT THE MECHANISM OF THE
EXPLOSIVE DECOMPOSITION OF HEAVY METAL AZIDES

It is widely assumed that the energetics of decomposition (including explosive ones!) is related to an exothermic
reaction

\[ 2N_3(2\Pi_g) \rightarrow 3N_2(1\Sigma_g^+) , \]  

(1)

which evolves an energy \( Q = 8.8 \text{ eV} \) [2].

It should immediately be emphasized that the value of \( Q \) is calculated for an isolated molecule. There is no direct
experimental support for the realization of the reaction (1) in the solid state, nor for the corresponding validity of the estimated
value of \( Q \). However, there are no other evident sources of energy which could cause the decomposition of the heavy metal
azides, other than the reaction (1). Therefore, this assumption lies at the basis of all the existing models of the decomposition
process.

How should we assume that the reaction (1) proceeds in the solid state? It is assumed that the ionization of the \( N_3^- \)
anion produces the radical \( N_0 \). Then the reaction (1) may be written in terms of radicals as

\[ 2N_0 \rightarrow 3N_2 , \]  

(2)

where it is typically assumed that the value of \( Q \) in this case is not much different from 8.8 eV (which is not obvious!).

In earlier work [1] it has been assumed that there is a real diffusion of \( N_0 \) radicals, which causes them to meet and
undergo the reaction (2). Therefore, it is assumed that the reaction (2) proceeds at the surface and even in a gas or liquid layer
close to the surface, where the diffusion process is facilitated. However, rather early on there was an understanding of the fact
that there is no necessity of \( N_0 \) radical diffusion in order for the reaction (2) to proceed. It is sufficient that the band holes and
localize within neighboring lattice sites of each other [2]. Then the reaction (2) would be rewritten in the band language as

\[ p + p \rightarrow 3N_2 , \]  

(3)

where \( p \) is a band hole.

We now turn our attention to the "translation fossils" which arise when we rewrite the reaction from the form (2) to
the form (3).

1. The hole is a delocalized state and therefore is not equivalent to the \( N_0 \) radical. The translation \( p \rightarrow N_0 \) corresponds
to a localized hole. Since there is no data on the self-localization of holes in heavy metal azides, the localization must occur
at a defect [4, 5]. The simplest candidate for this role is a cationic vacancy \( v_c \). The capture of holes at a cationic vacancy is
apparently accomplished sequentially: the first hole is trapped at a negatively charged center (\( \sigma \approx 10^{-13} \text{ cm}^2 \)), while the
second is trapped at the neutral one (\( \sigma \approx 10^{-15} \text{ cm}^2 \)) [5].

2. In the reaction (2) the radical \( N_0^2 \) disappears, however the translation in rewriting it as reaction (3), in which the
two holes "recombine" [3], violates the fundamentals of band theory, and, more broadly, fundamental conservation laws of
the number of particles and antiparticles [6]. Therefore, in the reaction (3) the holes do not disappear, but become localized
on a center which is reconstructed as a result of the reaction (2). Taking this discussion into account, we write (3) more
correctly as

\[ p + p + v_c \rightarrow (v_c)2p_l \rightarrow (v_c, 3N_2)2p_l \]  

(4)

where \( p_l \) is a hole localized on the defect.

The release of energy \( Q \), respectively by reaction (1) and in the case of the solid state reaction (4), takes place during
the reconstruction stage on the center: \( (v_c)2p_l \rightarrow (v_c, 3N_2)2p_l \). Thus, the localization of two holes on the defect leads to an
energy release \( Q \) which, according to the accepted point of view [2], is not much different from 8.8 eV. To what can we
attribute this fact?

The value of \( Q \) is substantially larger than the width of the band gap in the heavy metal azides (1.5 eV in \( \text{AgN}_3 \)) [6].
Consequently, the energy \( Q \) is sufficient to create new electron-hole pairs. This will increase the rate at which holes encounter

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